ELECTRONIC SUPPORTING INFORMATION

Dynamic Multivalent Recognition of Cyclodextrin Vesicles

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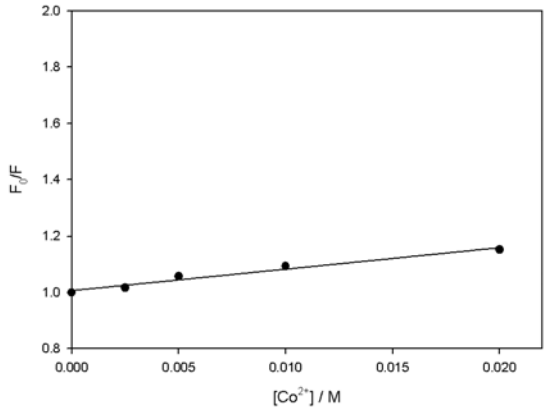
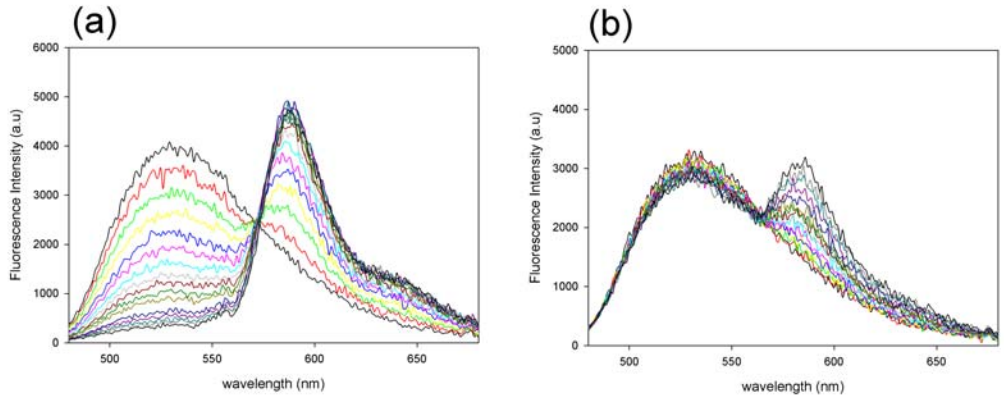
S-1. Location of NBD-Chol 2 in CD vesicles.

Co^{2+} is a powerful quencher for NBD fluorescence. However, if NBD is buried in a bilayer membrane, quenching by the hydrophilic Co^{2+} ion is not efficient. Chattopadhyay and London (*Biochim. Biophys. Acta*, **1998**, *938*, 24-34; *Biochemistry*, **1987**, *26*, 39-45) have proposed a correlation of the localization of NBD dyes in a bilayer membrane with the Co^{2+} quenching efficiency. Compared with their results, our experiments (K_{sv} = 8.09 ± 0.85 M^{-1}) show that the localization of NBD-Chol **2** in the CD vesicles is similar to the localization of NBD in 6-NBD-phosphatidyl choline and 12-NBD-phosphatidyl choline, indicating that NBD-Chol **2** resides deeply in the CD vesicle membrane.



Quenching (F/F_0) of NBD-Chol **2** in vesicles of β-CD **1b** by the addition of Co^{2+} ion. Experiments were carried out in 10mM Tris buffer, 150mM NaCl, pH = 7.2.

S-2. Addition of LRB-Ad2 3 and LRB to vesicles of cyclodextrin 1b



Fluorescence emission spectra (λ_{ex} = 450nm) of vesicles of β-CD **1b** (10 μM) containing 1 mol % NBD-Chol **2** (0.1 μM) upon adding (a) divalent guest LRB-Ad_2 **3** (b) lissamine rhodamine B (LRB). [LRB] = 0 - 0.9 μM for both experiments. All measurements were carried out in 5 mM phosphate buffer at pH = 7.5 and T = 25 °C.

S-3. Calculation of C_{eff} in CD vesicles

The effective concentration of cyclodextrin (C_{eff}) experienced by guest **3** on the surface of a mixed vesicle of CDs **1a** and **1b** was calculated from the following geometric considerations, in analogy with ref 7:

molecular surface area of α-CD **1a**: $A_{\alpha\text{-CD}} = 3.4 \times 10^{-18}$ m^2 (ref 3)

molecular surface area of β-CD **1b**: $A_{\beta\text{-CD}} = 3.75 \times 10^{-18}$ m^2 (ref 3)

fraction of α-CD **1a** in mixed vesicles: $f_{\alpha\text{-CD}}$

fraction of β-CD **1b** in mixed vesicles: $f_{\beta\text{-CD}}$

fraction of surface area covered by β–CD **1b**:

$$\sigma_{\beta\text{–CD}} = (f_{\beta\text{–CD}} \times A_{\beta\text{–CD}}) / (f_{\beta\text{–CD}} \times A_{\beta\text{–CD}} + f_{\alpha\text{–CD}} \times A_{\alpha\text{–CD}})$$

surface coverage of host sites:

$$\Gamma_{s,max}\ (100\%) = 1 / (N_{Av} \times A_{\beta\text{–CD}} \times 10000)\ (\text{mol cm}^{-2})$$

$$\Gamma_s = \sigma_{\beta\text{–CD}} \times \Gamma_{s,max}\ (100\%)$$

distance between adamantyls in **3**: $L = 3.49 \times 10^{-9}$ m from CPK model

effective concentration of CD:

(ref 7)

$$C_{eff,max} = \frac{\pi L^2 N_{Av} \Gamma_s - 1}{(^2/_3)\pi N_{Av} L^3}$$